New Simple Route to Prepare Dy₂Ce₂O₇ Nanostructures: Structural and Photocatalytic Studies

Zahra Salehi, Sahar Zinatloo-Ajabshir, Masoud Salavati-Niasari*

*Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167,
I. R. Iran*

* Corresponding author. Tel.: +98 31 55912383; Fax: +98 31 55913201; E-mail address:
salavati@kashanu.ac.ir (M. Salavati-Niasari)

Abstract: A novel approach of preparing nanostructured Dy₂Ce₂O₇ was developed utilizing the simple salt-assistant combustion way. For the first time, NaCl as dispersant as well as the mixtures of succinic acid and various amino acids as fuel and capping agent have been employed to produce nanostructured Dy₂Ce₂O₇. In this study, dysprosium nitrate and cerium(IV) ammonium nitrate were chosen as precursors. The grain size and morphology of Dy₂Ce₂O₇ may be controlled by alteration the kind of amino acid. The formation of as-synthesized nanocrystalline Dy₂Ce₂O₇ and its elemental composition, shape, structure and optical characteristics are analyzed utilizing UV-vis, FESEM, FT-IR, XRD, TEM and EDS. In addition, the photocatalytic performance of as-produced nanocrystalline Dy₂Ce₂O₇ was examined by degradation of eosin Y dye as water contaminant under ultraviolet light illumination.

Keywords: Dy₂Ce₂O₇; Photocatalytic; Nanostructures; Morphology-controlled; Optical.

1. Introduction

...One of the most attractive and effective rare earth materials is rare earth-doped cerium oxide materials that have excellent and substantial mechanical, electrical, catalytic and optical characteristics. Rare earth-doped cerium oxide materials have received a particular attention owing to their usages in the solid oxide

fuel cells (SOFC), oxygen sensors, catalyst carriers, photocatalyst and thermal barrier coatings [1-7]. Rare earth-doped cerium oxide has been synthesized through utilizing various routes including carbonate coprecipitation, citrate auto ignition, solid state reaction and combustion [8-14]. It is well known that the fundamental characteristics and ultimate uses of nanometer-scale materials extremely depend on their grain size and shape. Following this aim many efforts have been devoted to the size and morphology controlled fabrication of nanometer-scale materials [15-21]. Among the different approaches of production of nanometer-scale compounds, the combustion approach provides a cost-effective, reasonable and facile route to control and optimize the size and shape of the nanometer-scale materials.

Herein, nanostructured $\text{Dy}_2\text{Ce}_2\text{O}_7$ is prepared via a simple salt-assistant combustion way by utilizing the mixtures of succinic acid and various amino acids as fuel, dysprosium nitrate and cerium(IV) ammonium nitrate as precursors as well as NaCl as dispersant. To our knowledge, investigations on the production of nanostructured $\text{Dy}_2\text{Ce}_2\text{O}_7$ by applying the mixtures of succinic acid and various amino acids as fuel as well as NaCl as dispersant have not been documented to date. This study has provided a reliable, cost-effective, facile, reproducible, and quick procedure to optimize the shape and particle size of the nanostructured $\text{Dy}_2\text{Ce}_2\text{O}_7$.

2. Experimental

2.1 Materials and characterization

In this study, all reagents employed for the production of nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ were of analytical grade and were exploited as received. Thermogravimetric-differential thermal curve (TG-DTA) of the as-obtained sample was obtained by employing a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min^{-1} and a heating rate of $10^\circ \text{C min}^{-1}$. The EDS analysis of the as-produced nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was done by employing a Philips XL30 microscope. The UV-vis

diffuse reflectance analysis of the as-produced nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was done by employing a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). XRD analysis of the as-synthesized nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was carried out by employing a diffractometer of Philips Company with X'Pert Promonochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The morphological characteristics of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was investigated by TEM (JEM-2100) and FESEM (Mira3 Tescan). Fourier transform infrared analysis of as-obtained products was done by employing a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the $400\text{--}4000 \text{ cm}^{-1}$ range.

2.2 Preparation of nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$

The nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was prepared by the simple salt-assistant combustion route. A certain quantity of fuel (mixture of succinic acid and phenylalanine) was dissolved in distilled water. A solution including 1 mmol of dysprosium nitrate, 1 mmol of cerium(IV) ammonium nitrate and 2 mmol of NaCl was added into the mixture of succinic acid and phenylalanine solution (succinic acid: phenylalanine molar ratio of 1:2) under strong magnetic stirring. The mixed solution was heated at 60°C for 50 min under vigorous stirring. Then the obtained solution was allowed to evaporate. Finally, to prepare the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$, the obtained powders were dried at 110°C and calcined at 700°C for 4 h (sample no. 1). [Scheme 1](#) reveals the schematic diagram of the preparation pathway of nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$. Besides, the influence of the kind of amino acid on the grain size and morphology of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ were evaluated and the achieved results depicted in [Table 1](#). ([Table 1](#)).

2.3 Photocatalytic test

The photocatalytic behavior of the $\text{Dy}_2\text{Ce}_2\text{O}_7$ (sample nos.1 and 5) and CeO_2 (sample no.9) was determined by the photooxidation of eosin Y solution ($\text{pH} = 5$) as an objective pollutant. The reaction

solution containing the 15 mg of the eosin Y and 60 mg of the products in the quartz reactor was employed to determine the photocatalytic behavior. After aerating for 30 min in darkness to achieve the adsorption–desorption equilibrium, the final mixture was irradiated at 365 nm by the UV light (400 W high pressure mercury lamps). The eosin Y dye photooxidation efficiency was calculated as follow:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance quantity of eosin Y dye solution before and after photooxidation by means of a UV–vis spectrometer.

3. Results and discussion

[Fig. 1](#) reveals thermogravimetry (TG) of as-synthesized powders (sample no. 1 before calcination at 700 °C). As depicted in [Fig. 1](#), a total of three mass losses were seen. A mass loss happens between 25 and 230 °C (exhibiting 3 % mass loss), and this mass loss is indicative of the vaporization of the surface moisture. The other happened mass loss stages at the 230–700 °C (showing 75 % mass loss) can be assigned to the auto-ignition stages and confirm the combustion production and the removal of the residual combustible carbon, and the synthesis of nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$. To prove the purity level of the as-synthesized nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ (sample no. 1), EDS analysis was performed ([Fig. 2a](#)). This figure depicts only the presence of Ce, Dy, and O elements in the nanocrystalline sample and production of $\text{Dy}_2\text{Ce}_2\text{O}_7$.

The average crystallite diameter and crystal phase of the as-produced nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ (sample no. 1) were determined by XRD analysis. XRD pattern of the sample no. 1 prepared utilizing the mixture of succinic acid and phenylalanine is illustrated in [Fig. 2b](#). The XRD pattern of the nanocrystalline sample reveals the production of pure fluorite $\text{Dy}_2\text{Ce}_2\text{O}_7$ [9]. By employing Scherrer

equation [18], the average crystallite diameter of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ (sample no. 1) from the XRD data was determined to be about 28 nm.

The surface of the sample no. 1 before and after calcination step was evaluated by FTIR analysis. Fig. 3a and b reveals the infrared spectra. The peak centered at 788 cm^{-1} in the FT-IR spectrum of the sample no. 1 before calcination step (Fig. 3a) is assigned to the bending vibration of ionic CO_3^{2-} , which formed by the hydrolysis of the phenylalanine amino acid [22]. In this spectrum (Fig. 3a), the peaks centered at 1412 and 1061 cm^{-1} are attributed to the vibration modes of the NH_2 and CN groups [22], which demonstrates the existence of the unreacted phenylalanine amino acid in the sample no. 1 before calcination step. In the FT-IR spectrum of the sample no. 1 after calcination step (Fig. 3b), the peaks located at 3430 and 1629 cm^{-1} can be attributed to the surface adsorbed H_2O molecules [19]. In this spectrum (Fig. 3b), the characteristic peaks of the $\text{Dy}_2\text{Ce}_2\text{O}_7$ appear at 1026 and 503 cm^{-1} [23, 24].

The detailed morphological features of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ sample prepared by employing the mixture of phenylalanine and succinic acid as fuel in the presence of NaCl as dispersant are given in the TEM micrographs of Fig. 4a-c. TEM micrographs reveal that the $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles are mainly sphere-like with diameters of 19-29 nm.

...To evaluate the effect of the kind of amino acid parameter on the grain size and morphology of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$, FESEM analysis was utilized. For examining the influence of the kind of amino acid parameter on the morphology and grain size, the $\text{Dy}_2\text{Ce}_2\text{O}_7$ samples were synthesized by employing the mixture of succinic acid and phenylalanine (sample no. 1), valine (sample no. 2), serine (sample no. 3), L-alanine (sample no. 4) and glycine (sample no. 5) as fuel. FESEM images of sample nos. 1-5 prepared by the mixtures of succinic acid and various amino acids as fuel are depicted in Fig. 5a-e. As demonstrated in Fig. 5a-e, by applying the mixture of succinic acid and phenylalanine (Fig. 5a),

valine (Fig. 5b), serine (Fig. 5c), L-alanine (Fig. 5d) and glycine (Fig. 5e) as fuel, the nanoparticles with uniform sphere-like shape, the nanostructures composed of nanobundles, the coalesced particles/irregular microstructures, not uniform micro-spherical structures and irregular bulk structures are produced, respectively. These utilized amino acid kinds with various steric hindrance influence may act as both co-capping agent and fuel. It seems that these amino acid kinds as co-capping agent may supply the various reaction interfaces and cause the formed nanoparticles to assemble in the specific directions. As a result, $\text{Dy}_2\text{Ce}_2\text{O}_7$ samples with various morphologies were prepared. Among these amino acid kinds, phenylalanine provides the greatest steric hindrance influence. It plays a co-capping agent role via impeding the aggregation of the prepared nanoparticles. Besides, FESEM micrographs demonstrate that the reduction in the steric hindrance effect causes the enhancement in the grain size (Fig. 5a-e). It seems that the nucleation stage to be occurred rather than the particle growth stage via raising the steric hindrance influence. Based on the morphological studied of the as-produced $\text{Dy}_2\text{Ce}_2\text{O}_7$ samples, the most favorable and effective amino acid kind in presence of succinic acid for uniform sphere-like nanoparticles is phenylalanine (Fig. 5a).

Moreover, the effect of the NaCl as dispersant on the shape and size of $\text{Dy}_2\text{Ce}_2\text{O}_7$ was examined (Fig. 6a). To investigate the influence of this factor, an experiment was done in absence of the NaCl (sample no. 6). The sample no. 6 exhibits the high agglomerated particles structures (Fig. 6a). NaCl as dispersant precipitates and melts on the outer surface of the obtained nanoparticles and impedes from the sintering of the produced nanoparticles [25]. It can be found that employing NaCl as dispersant in presence of the mixture of succinic acid and phenylalanine leads to synthesize the homogeneous sphere-like $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles (Fig. 5a).

To study the effect of the phenylalanine amino acid on the morphology and grain size, the sample no. 7 was synthesized in the absence of phenylalanine amino. FESEM image of this sample is depicted in Fig.

6b. It is noteworthy that irregular micro/nanostructures with large grain size were obtained. The phenylalanine amino acid as fuel with great steric hindrance influence can act as a co-capping agent. It is apparent that the applying phenylalanine amino acid in presence of succinic acid and NaCl causes that the fluorite $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles with uniform sphere-like morphology are produced (Fig. 5a and 6b).

Moreover, the effect of the succinic acid as complexing agent on the morphology and grain size of $\text{Dy}_2\text{Ce}_2\text{O}_7$ was examined (Fig. 6c). To study the influence of the succinic acid parameter, on reaction was done without applying the succinic acid (sample no. 8). This sample reveals reveal irregular micro/nanostructures with large particle size (Fig. 6c). It seems that the succinic acid with great chelating effect plays a complexing agent role and controls growth of obtained nanoparticles. It is apparent that utilizing succinic acid as a complexing agent in presence of phenylalanine leads to synthesize homogenous sphere-like $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles (Fig. 5a). Thus, the excellence of applying succinic acid is that it causes to $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles with uniform spherical morphology.

To evaluate the optical features of the as-produced $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles (sample no. 1), UV–vis diffuse reflectance spectroscopy was utilized. Fig. 7a depicts the UV–vis diffuse reflectance spectrum of the sample no. 1. The absorption band appears at 348 nm in the spectrum of $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles. It is well known that the photocatalytic features of the nanometer-scale materials mainly depend upon the energy gap (E_g) parameter. This great factor may be determined based on the UV–vis diffuse reflectance result applying Tauc's formula [17]. The E_g of the $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles was estimated through extrapolating the linear section of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the energy axis (Fig. 7b). The E_g quantity of the $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles was calculated to be 3.3 eV. Based on the determined E_g amount, it is found that the as-synthesized $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles (sample no. 1) may be applied as the photocatalyst.

...The photooxidation of eosin Y dye experiment under ultraviolet light was done to examine the photocatalytic features of the as-synthesized Dy₂Ce₂O₇ (sample nos. 1 and 5 with various morphologies) and CeO₂ (sample no. 9). The results of the photocatalytic tests are depicted in Fig. 7c. No eosin Y was practically decomposed after 1 h in absence of the ultraviolet light illumination or the as-synthesized Dy₂Ce₂O₇ (sample nos. 1 and 5) and CeO₂ (sample no. 9). This result demonstrated that the contribution of self-decomposition was negligible. The BET-plot (adsorptive N₂) of the sample no. 1 is illustrated in Fig. 7d. The BET surface area of the sample no. 1 was determined to be about 13.03 m²g⁻¹. The proposed mechanism of the decomposition of eosin Y may be assumed as:

Based on the photocatalytic calculations by means of Eq. (1), the eosin Y dye decomposition was about 87, 60 and 54 % over sample nos. 1, 5 and 9, respectively, after 60 min irradiation of ultraviolet light and the as-synthesized Dy₂Ce₂O₇ nanoparticles (sample no. 1) revealed better photocatalytic performance than the sample nos. 5 and 9. The obtained results indicate that the Dy₂Ce₂O₇ nanoparticles with uniform sphere-like shape and small particle size (sample no. 1) have very good potential to be applied as desirable and efficient material for photocatalytic usages under ultraviolet light illumination. In the

heterogeneous photocatalytic processes, there are the diffusion, adsorption and reaction steps. It is well known that photocatalytic features depends dramatically on the diffusion of reactants and products, and thus the desirable distribution of the pore. It seems that the great photocatalytic performance of the as-produced $\text{Dy}_2\text{Ce}_2\text{O}_7$ nanoparticles can be corresponding to the desirable distribution of the pore, great hydroxyl amount and the fast separation of the charge carriers [26] (Fig. 7e).

4. Conclusions

This work describes a facile salt-assistant combustion route to synthesize the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ with the aid of dysprosium nitrate and cerium(IV) ammonium nitrate as precursors, the mixtures of succinic acid and various amino acids as fuel as well as NaCl as dispersant. Utilizing of the mixtures of succinic acid and different amino acids as fuel in presence of NaCl as dispersant is the novelty of this research. $\text{Dy}_2\text{Ce}_2\text{O}_7$ samples with the different shapes and particle sizes were obtained via alteration the kind of amino acid. When as-synthesized nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$ was applied as photocatalyst, the eosin Y decomposition percentage was about 87 after 60 min illumination of ultraviolet light. This obtained result suggests as-produced $\text{Dy}_2\text{Ce}_2\text{O}_7$ as an interesting and efficient candidate for photocatalytic usages under ultraviolet light. This study suggests a new, reliable, cost-effective and facile process for the production of the nanocrystalline $\text{Dy}_2\text{Ce}_2\text{O}_7$.

Acknowledgements

Authors are grateful to the council of Iran National Science Foundation (91053846) and University of Kashan for supporting this work by Grant No (159271/820).

References

- [1] J. S. Bae, W. K. Choo, Ch. H. Lee, The crystal structure of ionic conductor $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$, J. Eur. Ceram. 24 (2004) 1291–1294.
- [2] Y. Wang, H. Guo, Sh. Gong, Thermal shock resistance and mechanical properties of $\text{La}_2\text{Ce}_2\text{O}_7$ thermal barrier coatings with segmented structure, Ceram. Int. 35 (2009) 2639–2644.
- [3] W. M. O'Neill, M. A. Morris, The defect chemistry of lanthana–ceria mixed oxides by MASNMR, Chem. Phys. Lett. 305 (1999) 389–394.
- [4] V. Besikiotis, Ch. S. Knee, I. Ahmed, R. Haugsrud, T. Norby, Crystal structure, hydration and ionic conductivity of the inherently oxygen-deficient $\text{La}_2\text{Ce}_2\text{O}_7$, Solid State Ionics 228 (2012) 1–7.
- [5] E. Y. Pikalova, A. A. Murashkina, V. I. Maragou, A. K. Demin, V. N. Strekalovsky, P. E. Tsiakaras, CeO_2 based materials doped with lanthanides for applications in intermediate temperature electrochemical devices, Int. J. Hydrogen Energy 36 (2011) 6175–6183.
- [6] Ch. Wang, Y. Wang, A. Zhang, Y. Cheng, F. Chi, Zh. Yu, The influence of ionic radii on the grain growth and sintering-resistance of $\text{Ln}_2\text{Ce}_2\text{O}_7$ (Ln = La, Nd, Sm, Gd), J. Mater. Sci. 48 (2013) 8133–8139.
- [7] S. Kuharuangrong, Ionic conductivity of Sm, Gd, Dy and Er-doped ceria, J. Power Sources 171 (2007) 506–510.
- [8] J. J. G. Li, T. Ikegami, T. Mori, T. Wada, Reactive $\text{Ce}_{0.8}\text{RE}_{0.2}\text{O}_{1.9}$ (RE = La, Nd, Sm, Gd, Dy, Y, Ho, Er, and Yb) Powders via Carbonate Coprecipitation, Chem. Mater. 13 (2001) 2913–2920.
- [9] Zh. Hongsong, L. Suran, G. Shaokang, Preparation and Thermal Conductivity of $\text{Dy}_2\text{Ce}_2\text{O}_7$ Ceramic Material, JMEPEG 21 (2012) 1046–1050.

- 212 [10] A. K. Baral, V. Sankaranarayanan, Ionic Transport Properties in Nanocrystalline $\text{Ce}_{0.8}\text{A}_{0.2}\text{O}_{2-\delta}$ (with
213 $\text{A} = \text{Eu, Gd, Dy, and Ho}$) Materials, *Nanoscale. Res. Lett.* 5 (2010) 637–643.
- 214 [11] Y. Y. P. Fu, S. H. Chen, F. Y. Tsai, Sh. H. Hu, Aqueous tape casting and crystallization kinetics of
215 $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{1.9}$ powder, *Ceram. Int.* 35 (2009) 609–615.
- 216 [12] Zh. Zhu, L. Yan, H. Liu, W. Sun, Q. Zhang, W. Liu, A mixed electronic and protonic conducting
217 hydrogen separation membrane with asymmetric structure, *Int. J. Hydrogen Energy* 37 (2012) 12708–
218 12713.
- 219 [13] H. Zhang, S. Liao, X. Dang, Sh. Guan, Zh. Zhang, Preparation and thermal conductivities of
220 $\text{Gd}_2\text{Ce}_2\text{O}_7$ and $(\text{Gd}_{0.9}\text{Ca}_{0.1})_2\text{Ce}_2\text{O}_{6.9}$ ceramics for thermal barrier coatings, *J. Alloys Compd.* 509 (2011)
221 1226–1230.
- 222 [14] W. Sun, S. Fang, L. Yan, W. Liu, Investigation on Proton Conductivity of $\text{La}_2\text{Ce}_2\text{O}_7$ in Wet
223 Atmosphere: Dependence on Water Vapor Partial Pressure, *Fuel Cells* 12 (2012) 457–463.
- 224 [15] S. Zinatloo-Ajabshir, M. Salavati-Niasari, Synthesis of pure nanocrystalline ZrO_2 via a simple
225 sonochemical-assisted route, *J. Ind. Eng. Chem.* 20 (2014) 3313–3319.
- 226 [16] S. Moshtaghi, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Nanocrystalline barium stannate: facile
227 morphology-controlled preparation, characterization and investigation of optical and photocatalytic
228 properties, *J. Mater. Sci.: Mater. Electron.* 27 (2016) 834–842.
- 229 [17] S. Zinatloo-Ajabshir, M. Salavati-Niasari, Novel poly(ethyleneglycol) assisted synthesis of
230 praseodymium oxide nanostructures via a facile precipitation route, *Ceram. Int.* 41 (2015) 567–575.

- [18] S. Mortazavi-Derazkola, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Novel simple solvent-less preparation, characterization and degradation of the cationic dye over holmium oxide ceramic nanostructures, *Ceram. Int.* 41 (2015) 9593–9601.
- [19] S. Zinatloo-Ajabshir, M. Salavati-Niasari, M. Hamadani, Praseodymium oxide nanostructures: novel solvent-less preparation, characterization and investigation of their optical and photocatalytic properties, *RSC Adv.* 5 (2015) 33792–33800.
- [20] S. Mortazavi-Derazkola, S. Zinatloo-Ajabshir, M. Salavati-Niasari, New sodium dodecyl sulfate-assisted preparation of Nd_2O_3 nanostructures via a simple route, *RSC Adv.* 5 (2015) 56666–56676.
- [21] F. Beshkar, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Simple morphology-controlled fabrication of nickel chromite nanostructures via a novel route, *Chem. Eng. J.* 279 (2015) 605–614.
- [22] B. Wang, R. Yan, D. H. Lee, Y. Zheng, H. Zhao, Ch. Zheng, Characterization and evaluation of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier prepared by sol–gel combustion synthesis, *J. Anal. Appl. Pyrolysis* 91 (2011) 105–113.
- [23] C. E. Jeyanthi, R. Siddheswaran, R. Medlín, M. K. Chinnu, R. Jayavel, K. Rajarajan, Electrochemical and structural analysis of the $\text{RE}^{3+}:\text{CeO}_2$ nanopowders from combustion synthesis, *J. Alloys Compd.* 614 (2014) 118–125.
- [24] N. Krishna Chandar, R. Jayavel, Wet chemical synthesis and characterization of pure and cerium doped Dy_2O_3 nanoparticles, *J. Phys. Chem. Solids* 73 (2012) 1164–1169.
- [25] W. Chen, F. Li, J. Yu, L. Liu, A facile and novel route to high surface area ceria-based nanopowders by salt assisted solution combustion synthesis, *Mater. Sci. Eng., B* 133 (2006) 151–156.

251 [26] J. Zhong, J. Li, F. Feng, Y. Lu, J. Zeng, W. Hu, Z. Tang, Improved photocatalytic performance of
252 $\text{SiO}_2\text{--TiO}_2$ prepared with the assistance of SDBS, J. Mol. Catal. A: Chem. 357 (2012) 101–105.

253

254

255 **Table 1.** The preparation conditions of the samples synthesized in this study.

Sample No.	Amino acid kind	Succinic acid	NaCl	Dy:Ce	Figure of FESEM images
1	Phenylalanine	+	+	1:1	5a
2	Valin	+	+	1:1	5b
3	Serine	+	+	1:1	5c
4	L-Alanine	+	+	1:1	5d
5	Glycine	+	+	1:1	5e
6	Phenylalanin	+	-	1:1	6a
7	-	+	+	1:1	6b
8	Phenylalanine	-	+	1:1	6c
9	Phenylalanine	+	+	0:1	-

256

257

258 **Figure Captions:**

259 **Figure 1.** TGA curve of the as-synthesized powders (sample no. 1 before calcination at 700 °C).

260 **Figure 2.** EDS (a) and XRD (b) patterns of the as-produced nanocrystalline Dy₂Ce₂O₇ (sample no. 1).

261 **Figure 3.** FT-IR spectra of the sample no. 1 before (a) and after (b) calcination step.

262 **Figure 4.** TEM images of the nanocrystalline Dy₂Ce₂O₇ (sample no. 1).

263 **Figure 5.** FESEM images of the sample nos. 1, 2, 3, 4 and 5 prepared applying the mixtures of succinic
264 acid and phenylalanine (a), valine (b), serine (c), L-alanine (d) and glycine (e) as fuel.

265 **Figure 6.** FESEM images of the samples prepared without applying the NaCl (a), phenylalanine (b) and
266 succinic acid (c).

267 **Figure 7.** UV-vis diffuse reflectance spectrum (a), plot to determine the band gap (b) of as-produced
268 nanocrystalline Dy₂Ce₂O₇ (sample no. 1), photocatalytic eosin Y degradation of as-synthesized Dy₂Ce₂O₇
269 (sample nos. 1 and 5) and CeO₂ (sample no. 9) at pH = 5 (c), BET-plot of as-obtained nanocrystalline
270 Dy₂Ce₂O₇ (sample no. 1) (d), and reaction mechanism of eosin Y photooxidation over Dy₂Ce₂O₇ (sample
271 no. 1) under ultraviolet light illumination (e).

272 **Scheme 1.** Schematic diagram of the preparation of the nanocrystalline Dy₂Ce₂O₇.

273

274

275 **Scheme 1.**

276

277

278 **Fig 1.**

279

280

281 **Fig 2.**

282

283

284 **Fig 3.**

285

288 **Fig 4.**

293

294 **Fig 6.**

295

296 **Fig 7.**

297

298

299